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(21) International Application Number: PCT/DK86/00063 (22) International Filing Date: 11 June 1986 (11.06.86) (31) Priority Application Number: 2944/85 (32) Priority Date: 28 June 1985 (28.06.85) (33) Priority Country: DK  (71) Applicant (for all designated States except US): SPAROL INTERNATIONAL APS [DK/DK]; Trollesgave, Fensmark, DK-47000 Næstved (DK). (72) Inventor; and (75) Inventor/Applicant (for US only) : JACOBSEN, Niels, Knud, Erik [DK/DK]; Trollesgave, Fensmark, DK-4700 Næstved (DK). (74) Agent: CHAS. HUDE; 33, H.C. Andersens Boulevard, DK-1553 Copenhagen V (DK).			(81) Designated States: AT (European patent), AU, BE (European patent), BR, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), IT (European patent), JP, KP, KR, LK, LU (European patent), MC, ML (OAPI patent), MR (OAPI patent), NL (European patent), NO, RO, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.  Published With international search report.
(54) Title: AN ADDITIVE FOR LIQUID FUEL			
(57) Abstract			
<p>An additive for liquid fuel, such as fuel oil, gas oil and Diesel oil comprising manganese salts of aliphatic acids, high-boiling tar oil and naphthalene as compulsory ingredients and if necessary furthermore one or several of the ingredients, iron naphthenate, ferric chloride and calcium salts of aliphatic acids. The additive improves the combustion and consequently the efficiency, reduces accumulation and deposit of impurities in the combustion system, reduces environmental contaminating discharges and diminishes corrosion damages caused by acid ingredients, such as sulphuric acid.</p>			

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Title: An Additive for Liquid FuelTechnical Field

The present invention relates to an additive for liquid fuel, such as fuel oil, gas oil and Diesel oil, including 5 motor Diesel.

Background Art

For many years attempts have been made to find suitable agents which by addition to liquid fuels improve the combustion, reduce corrosion damages and diminish the accumulation of impurities in the system. 10

Furthermore, considerable amounts of additive for liquid fuels have been sold and used for many years, but unfortunately the effects obtained have not been satisfactory. A certain soot and oil coke reducing effect has, however, 15 been obtained by means of certain metals.

In order to reduce the formation of sulphuric acid and consequently the corrosion it is advantageous to work with a very small excess of air. An additional reason for aiming at combustion of oils at a very low excess of air is the 20 resulting considerable improvement of the efficiency. Unfortunately, a low excess of air results in formation of soot and oil coke in large amounts.

Disclosure of the Invention

It is the object of the present invention to provide a 25 new additive, which is better than the previously known additives, and which, with economical profits for the user, improves the combustion and consequently the efficiency, reduces accumulation and deposit of impurities in the combustion system, reduces environmental contaminating dis-

charges and reduces corrosion damages caused by acid ingredients, such as sulphuric acid.

This object is obtained by means of an additive for liquid fuel according to the invention and characterised by containing

- 1) manganese salts of aliphatic acids,
- 2) high-boiling tar oil, and
- 3) naphthalene

and if desired one or several of the following additional ingredients

- 4) iron naphthenate,
- 5) ferric chloride and
- 6) calcium salts of aliphatic acids.

As examples of applicable manganese salts may be mentioned  
15 manganese salts of branched aliphatic acids with 8-9 carbon atoms, such as Manganese Siccato<sup>®</sup> from Akzo Chemie, containing about 10% Mn, 61-67% of a non-volatile material as well as 35% of mineral spirits (white spirits) or "Nuodex<sup>®</sup> Dryer Manganese".

20 "Nuodex<sup>®</sup> Dryer Iron" may be mentioned as an example of a suitable iron naphthenate preparation.

Examples of suitable qualities of high-boiling tar oil may be those containing polyaromatic hydrocarbons, such as anthracene oil. By heating anthracene oil 40% are distilled  
25 in the temperature range 330-400°C. The flash point of anthracene oil is 180° in a closed cup.

Calcium salts of branched aliphatic acids with 8-9 carbon atoms, such as Calcium Siccato<sup>®</sup> from Akzo Chemie, containing about 5% Ca, 47-52% of non-volatile ingredients  
30 and mineral spirits as the remainder of "Nuodex<sup>®</sup> Dryer

Calcium" may be mentioned as suitable calcium salts of aliphatic acids.

An additive according to the invention may be prepared from the above three compulsory ingredients by heating separately the tar oil until it is liquid and by adding the naphthalene during continuous heating to form a homogeneous liquid mixture, which is thereafter mixed with the manganese salt preparation.

An additive according to the invention with all six ingredients is prepared by combining a mixture formed by stirring of the calcium salt preparation, the manganese salt preparation and the iron naphthenate preparation with a separately prepared melt mixture of tar oil, ferric chloride and naphthalene.

Before the additive products are marketed kerosine is usually added in order to obtain a stable mixture more easily compatible with the fuel.

The mixture proportion of the ingredients is normally within the following intervals for the used preparations with a content of the specified active ingredients:

25	1)	preparation containing manganese salts of aliphatic acids	10-100	1
	2)	high boiling tar oil	1-3	1
	3)	naphthalene	5-15	kg
	4)	iron naphthenate preparation	0-90	1
	5)	ferric chloride	0-5	kg
	6)	preparation containing calcium salts of aliphatic acids	0-80	1

Calculated on the contents of the active ingredients in the fuel it is assumed that the mixture proportion is as follows; it is, however, emphasized that the calculations

are subject to some uncertainty and should only be considered to be illustrating:

- |    |    |   |                        |
|----|----|---|------------------------|
|    | 1) | manganese salts of aliphatic acids (calculated as Mn)       | 0.008-0.08 kg/ton fuel |
| 5  | 2) | high-boiling tar oil  | 0.009-0.09 kg/ton fuel |
|    | 3) | naphthalene   | 0.04 -0.12 kg/ton fuel |
|    | 4) | iron naphthenate preparation (calculated as Fe-content)     | 0-0.05 kg/ton fuel     |
|    | 5) | ferric chloride   | 0-0.04 kg/ton fuel     |
| 10 | 6) | calcium salts of aliphatic acids (calculated as Ca-content) | 0-0.03 kg/ton fuel     |

A mixture of all six ingredients is normally used for the combustion of fuel oil.

15 An additive with no content of component 6) is normally used for the combustion of gas oil.

An additive with no content of component 6) is normally used for the combustion of Diesel oil and in case of addition to motor Diesel oil. However, in some cases the  
20 addition of a smaller amount of calcium salts of aliphatic acids may be preferred, whereby a loosening of deposits, including hard deposits, in the entire machinery is obtained.

The additive according to the invention is supposed to  
25 function in such a manner that it reduces the surface tension of the fuel, and as a result a better atomization and thus a better operation with fewer interruptions are obtained.

The reason for soot formation in connection with the com-  
30 bustion of liquid fuel is supposed to be that the atomized fuel drops are too big. Consequently, they cannot be burned

completely and pass in partly unburned condition through the boiler and are deposited in tubes and on other heat surfaces in the form of soot. Oil coke is also formed on account of too big fuel drops, as the oil in these drops  
5 are heated to a temperature, at which they can coke before the drop is burned out. The oil coke particles formed cannot burn under the prevailing conditions and are consequently carried with the exhaust gas. A finer atomization of the fuel is obtained by using the inventive additive,  
10 whereby a far more complete combustion is ensured than the one obtained when the fuel is burned in the form of bigger drops. By atomization of finer drops the complete combustion is ensured by the fact that a high temperature is maintained more easily throughout in the formed small  
15 drops. The lower temperature existing in the centre of bigger drops during the combustion thereof is consequently avoided. The complete combustion ensures that unburned impurities do not pass through the system, and protection against deposits as well as against contaminating dis-  
20 charges is thus achieved. The effective atomization of the fuel renders it possible to operate with reduced supply of air without thereby preventing the complete combustion. By means of the reduced supply of air an increased CO<sub>2</sub>-content is obtained in the exhaust gas, which characterises  
25 optimum combustion and efficiency.

In connection with the use of the additive according to the invention for fuel oil one liter of kerosine-containing additive is usually added to one ton of fuel oil. In case of such addition it is possible to reduce the temperature,  
30 to which the oil is normally preheated before combustion. This preheating is normally performed by electric heating and is expensive. The energy saving obtained per se will be of such a magnitude that it covers the costs of the additive.

35 It may in certain cases be desirable to avoid a reduction



of the preheating temperature, a more complete combustion with consequent "better results in the boiler" being obtained instead.

The use of the additive according to the invention in  
5 systems for combustion of fuel oil results in a reduction of the formation of soot, oil coke, clinkers and sulphuric acid. Protection against formation of heat-insulating coatings in the boiler with a consequent high efficiency is thus obtained. The corrosion damages on the exhaust gas  
10 side are furthermore reduced, and any water, if present, is emulsified in the oil. As a result a clean and dry boiler with a longer life is obtained, and the system is more stable in operation and requires less maintenance.

One liter of kerosine-containing additive per ton of oil  
15 is also used when the inventive additive is added to gas oil. The additive prevents development of paraffin wax, keeps tanks, tubes and filters clean, emulsifies water, if present, in the oil or water formed by condensation, and protects against corrosion. The additive affords pro-  
20 tection against frost down to  $-18^{\circ}\text{C}$ . A better atomization and thus a more complete combustion are ensured, whereby deposit of soot and coke is avoided. The more clean combustion reduces the fuel consumption and the wear and tear in connection with use in Diesel engines.

25 The additive according to the invention is also suitable for addition to Diesel oil used in stationary as well as mobile Diesel engines, e.g. marine engines. One liter of kerosine-containing additive is usually added per ton of Diesel oil. The additive prevents development of paraffin  
30 wax, gives a more clean engine and facilitates the starting. The additive affords protection against frost down to  $-18^{\circ}\text{C}$ . Tanks, tubes and filters are kept clean. The additive emulsifies any water present in the Diesel oil and water formed by condensation. Protection against cor-



rosion in tanks, tubes, pumps and valves is thus obtained. An improved atomization with consequent more complete combustion is achieved, which means that soot and coke deposits are avoided. As a result a reduction of the fuel consumption and less wear in Diesel engines is obtained.

### Examples

The invention will be described more detailed below with reference to the subsequent examples and tests.

#### Example 1

10 Preparation of an additive for fuel oil.

40 l (about 36.8 kg) of Calcium Siccato<sup>®</sup> (containing about 1.825 kg Ca), 20 l (about 20 kg) Manganese Siccato<sup>®</sup> (containing about 2 kg Mn) and 20 l (about 24 kg) of the iron naphthenate preparation "Nuodex<sup>®</sup> Dryer Iron" are  
15 combined by stirring with a separately prepared melt mixture of 2 l (about 2.32 kg) "anthracene oil" (40% boils from 330 to 400°C), 1 kg of ferric chloride and 12 kg of naphthalene. The resulting mixture is cooled and mixed with 20 l of kerosine. One liter of this mixture is dosed  
20 as additive to 1 ton of fuel. Product data for this additive are:

Density:	0.96
Appearance:	brownish liquid
Flash point:	58°C
25 Storage durability:	unlimited.

#### Example 2

Preparation of an additive for gas oil.

40 l (about 40 kg) of Manganese Siccato<sup>®</sup> (containing about

4 kg Mn) and 40 l (about 48 kg) of the iron naphthenate preparation "Nuodex<sup>®</sup> Dryer Iron" are combined by stirring with a separately prepared melt mixture of 2 l (2.32 kg) "anthracene oil" (40% boils from 330 to 400°C), 1 kg of 5 ferric chloride and 12 kg of naphthalene. The resulting mixture is cooled and mixed with 20 liter of kerosine. One liter of this mixture is dosed as additive to 1 ton of fuel. Product data for this additive are:

10      Density:                      0.90  
         Appearance:                brownish liquid  
         Flash point:                55°C  
         Storage durability: unlimited.

### Example 3

Preparation of an additive for Diesel oil.

15 70 l (about 70 kg) of Manganese Siccato<sup>®</sup> (containing about 7 kg Mn) and 10 l (about 12 kg) of the iron naphthenate preparation "Nuodex<sup>®</sup> Dryer Iron" are combined by stirring with a separately prepared melt mixture of 2 l (2.32 kg) "anthracene oil" (40% boils from 330 to 400°C), 1 kg of 20 ferric chloride and 12 kg of naphthalene. The resulting mixture is cooled and mixed with 20 liter of kerosine. One liter of this mixture is dosed as additive to 1 ton of fuel. Product data for this additive are:

25      Density:                      0.85  
         Appearance:                brownish liquid  
         Flash point:                55°C  
         Storage durability: unlimited.

The surprising, advantageous effect obtained with additives according to the invention are supported by the following 30 tests:

Test 1

In the tests fuel oil containing one liter of the kerosine-containing additive prepared according to example 1 per ton of fuel oil was compared with fuel oil without additive.

The boiler was operated with 80% load and the boiler was not adjusted during the tests.

Two tests were performed without additive (test a and test b) and two tests with additive (test c and test d).  
10 The results obtained appear from the following table 1.

Table 1

Test		without additive		with additive	
		a	b	c	d
15 Exhaust gas temperature	°C	209	209	211	211
CO <sub>2</sub> -content	%	13.90	14.03	13.80	13.85
Fired amount of oil	g/h	211.6	211.6	211.6	211.6
Concentration of solids exhaust gas					
20 per kg of oil	g/kg	4.57	4.54	1.52	1.56
SO <sub>2</sub> -concentration in exhaust gas	mg/m <sup>3</sup> n, t	3960	4000	3930	3950
Soot number (Bacharach)		5	5	2	2
Dosage	0/00	0	0	1	1

25 Test 2

In a test corresponding to test 1, but with the use of an additive with 20 liters of Calcium Siccato<sup>®</sup> and with the addition of 50 liters of kerosine the results stated in table 2 were obtained

Table 2

10

Test		without additive	with additive
		e	f
Exhaust gas temperature	°C	210	210
5 CO <sub>2</sub> -contents	%	13.9	13.9
Fired amount of oil	kg/h	210	210
Concentration of solids in exhaust gas per kg of oil	g/kg	4.6	1.5
SO <sub>2</sub> -concentration in 10 exhaust gas	mg/m <sup>3</sup> <sub>n,t</sub>	3900	3600
Soot number (Bacharach)		5	2
Additive dosage	0/00	0	2

As it appears from tables 1 and 2 essential reductions are obtained in the emission of solids which together with the reduction in the soot number results in a better operating economy in the boiler system. The results are obtained without adjusting the burner, as it was merely intended to show the effect of the additive for reduction of the emission.

20 The emission during dosage of additive is below the threshold value of 2.5 g/kg of oil suggested by the Department of the Environment, and this indicates that a better operating economy (higher CO<sub>2</sub>-percentage) during normal daily operation can be obtained by readjusting the burner.

25 As mentioned the boiler was not adjusted during the tests, and it appears that the CO<sub>2</sub>-number obtained are in all essentials unchanged. The CO<sub>2</sub>-content may be optimized by a suitable adjustment of the boiler.

### Test 3

30 Three different fuel oil systems were tested without adding any kind of additive. The CO<sub>2</sub>-content in the exhaust gas

was measured to about 12.5% and the soot number (Bacharach) to about 5.

The same systems were tested with addition of 8% of water. The results were: CO<sub>2</sub>-content 13.5%. Soot number 3-4.

5 By adding additive according to example 1 (one liter of kerosine-containing additive per ton of oil) the following values were achieved: CO<sub>2</sub>-content of 14.5% and soot number of 2-3.

It should be noted that no adjustments were made during 10 the three tests.

It is well-known to increase the CO<sub>2</sub>-content by emulsifying water into liquid fuel. It appears that the additive according to the invention has an even better increasing effect on the CO<sub>2</sub>-content.

15 By avoiding the use of water the risk of calcareous deposits is reduced, whereby the maintenance is reduced.

A further advantage of the use of the additive according to the invention is that expensive emulsifying systems, as known in connection with the addition of water, are avoided, as the additive should only be poured into the 20 tank or be dosed in any other simple manner.

By using the additive according to the invention the normally frequent cleanings are avoided. Cleaning is practically unnecessary, and if cleaning should be desired, it 25 suffices to perform the cleaning when the system is stopped for other reasons.

In the tests performed the boilers were more clean after application of the additive according to the invention than before the start of the tests.

Test 4

A conventional gas oil system previously operated with a CO<sub>2</sub>-content in the exhaust gas of about 13% and a soot number of 1-2.

5 After using the additive according to example 2 (one liter per ton of gas oil) the system operated with a CO<sub>2</sub>-content of about 14.5% and a soot number of 0-1.

At his first call after the additive had been put into use the chimney sweeper, who had no knowledge of the use  
10 of the additive, remarked that the chimney was surprisingly completely dry, and that only a very small amount of solids had to be removed at the bottom of the chimney.

It could furthermore be ascertained that the boiler was comparatively noiseless and odourless in operation in  
15 contrast to previously, where no additive was used.

Test 5

An old Diesel-driven lorry had previously encountered starting problems, and normally the exhaust was reeking.

After addition of one liter of the additive according to  
20 example 3 per ton of Diesel oil it could after 8 hours driving be ascertained that the starting problems had ceased and the exhaust no longer reeked. It was furthermore clear that the lorry had a better traction.

Claims:

1. An additive for liquid fuel, c h a r a c -  
t e r i s e d by containing a combination of

- 1) manganese salts of aliphatic acids,
- 5 2) high-boiling tar oil,
- 3) naphthalene

in admixture with 0, 1 or several of the following ad-  
ditional ingredients .

- 4) iron naphthenate,
- 10 5) ferric chloride and
- 6) calcium salts of aliphatic acids.

2. An additive as claimed in claim 1, c h a r a c -  
t e r i s e d in that the manganese salts of aliphatic  
acids 1) are manganese salts of branched aliphatic acids  
15 with 8-9 carbon atoms, and that the high boiling tar oil  
2) is a high-boiling tar oil quality containing polyaro-  
matic hydrocarbons, of which tar oil 35-50%, preferably  
about 40% are distilled at temperatures up to 400°C.

3. An additive as claimed in claim 1 or 2 for fuel oil,  
20 c h a r a c t e r i s e d by containing all six ingre-  
dients.

4. An additive as claimed in claim 1 or 2 for gas oil,  
c h a r a c t e r i s e d by containing a combination of  
ingredients 1)-5).

25 5. An additive as claimed in claim 1 or 2 for Diesel  
oil, c h a r a c t e r i s e d by containing a combination  
of ingredients 1)-5).

6. An additive as claimed in claim 1 or 2 for Diesel



oil, characterised by containing all six ingredients.

7. An additive as claimed in claim 1, 2, 3, or 6, characterised by containing as ingredient 6) calcium salts of branched aliphatic acids with 8-9 carbon atoms.

8. An additive as claimed in claim 1, characterised in that the active ingredients are present in such amounts that after addition to the fuel the content per ton of fuel will be

0.008-0.08 kg of ingredient 1) calculated as Mn,

0.009-0.09 kg of ingredient 2)

0.04 -0.12 kg of ingredient 3),

0-0.05 kg of ingredient 4) calculated as Fe-content,

0-0.04 kg of ingredient 5), and


0-0.03 kg of ingredient 6) calculated as Ca-content.

9. An additive as claimed in claims 1-8, characterised by containing as ingredient 1) Manganese Siccato<sup>®</sup>.

10. An additive as claimed in claims 1-3, 6-8 or 9, characterised by containing as ingredient 4) "Nuodex<sup>®</sup> Dryer Iron" and/or as ingredient 6) Calcium Siccato<sup>®</sup>.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/DK86/00063

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *		
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Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT *</b>		
Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
Y	EP, A1, 0 078 249 (LANG & CO, CHEMISCH- TECHNISCHE PRODUCTE) 4 May 1983 see claims 1, 3-5 and page 6, lines 20-21 & AT, 373274 CA, 1188891	1
Y	DE, A1, 3 044 907 (RUHRCHEMIE AG) 3 June 1982 see the claims & SE, 8106921 FR, 2495180 JP, 57155293	1
Y	Patent Abstracts of Japan, Vol 7, No 155, C 175, abstract of JP 58-67 789, publ 1983-04-22	1
Y	US, A, 1 092 461 (A W SWANBERG) 7 April 1914 see claim 1	1
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